

increase in thickness with increase in temperature as particularly taught in the specification.

In the Action, the examiner has stated that the Tokoro patent "discloses a balance spring 30 made of carbon", whose "thermal expansion and thermal elastic coefficient specification are not set forth" (see paragraph 2). The examiner has then also stated that the Baur patent teaches that "to correct for temperature changes, the thermoelastic coefficient and the coefficient of thermal expansion of the spring is adjusted in relation to the thermal expansion coefficient of the balance to compensate for these changes" (see paragraph 2). While applicant does not necessarily agree with these statements and conclusion, they will be accepted for the sake of the argument at this time.

Next, in paragraph 3, the examiner notes that the above combination does not make claim 23 obvious, but the examine further states:

[w]ith respect to the added limitation pertaining to a negative coefficient of thermal expansion in the axial direction, carbon and carbon nanofibers are known to have a negative CTE in the axial direction and a positive CTE in a transverse direction. Thus, one of ordinary skill in the art, being aware of these properties of carbon nanofibers would select appropriate materials and CTE's to compensate for thermal variations in the system of Tokoro, as taught by Baur.

However, this statement is incorrect and no teaching or suggestion is provided for these specifically claimed features.

With respect to the assertion about carbon, as reference to any of a variety of scientific books, websites, or tables will show, such as shown in the attached copy titled "Thermal Expansion" from The Physics Hypertextbook, carbon (graphite) has a positive

coefficient of thermal expansion in both the axial ("||") and transverse ("⊥") directions.

Thus, that part of the examiner's assertion which applies to carbon is plainly incorrect.

With respect to carbon nanofibers, which are specifically taught in the Tokoro patent as being used for the balance spring, the CTEs in the axial and transverse direction (particularly the transverse direction) is more uncertain due to the difficulties in measuring changes in what is already a very small fiber. It is assumed in the art that carbon nanofibers behave in this respect like convention carbon fibers, but proof is not easy to obtain.

However, even assuming that carbon nanofibers have the same CTEs as the conventional carbon fibers used for the balance spring of the present invention and as claimed in claim 23, that does not result in the balance spring of the Tokoro patent reading or making obvious the particular CTE recitations in claim 23.

As noted in *The Applied Science, Inc.* website (copy attached), it is known that nanofibers can be used to reduce the CTE of a matrix material in which they are held. This is what is going on in the Tokoro patent - see paragraph [0046] which notes the composite resin material in which the nanofibers are held. In particular as noted in the Tokoro patent, the resin is "carbonated", i.e. carbonized, so that the final composite comprises nanofibers held in a carbon matrix (see paragraphs 21+). This carbon matrix has a positive CTE (as noted above - or see again the attached copy of The Physics Hypertextbook reference). It will also be noted that the Tokoro patent makes no mention of controlling the orientation of the nanofibers in the matrix (and indeed applicant is not aware of this being possible in a carbon matrix), so those of ordinary skill will have to assume that the composite in the Tokoro patent is isotropic; i.e., with an

even distribution of carbon nanofibers occupying all orientations. And this isotropic distribution must be contrasted with conventional carbon fibers of the present invention, which, because of their scale relative to the balance spring, can and do provide an anisotropic material (as particularly claimed).

Claim 23 specifies that the material of the balance spring "decreases in length and increases in thickness with an increase in temperature". To do this, the material must exhibit a negative CTE in the longitudinal direction and a positive CTE in the transverse direction, i.e., anisotropic behavior. In the Tokoro patent, the matrix is made of carbon, which has a positive CTE in all directions, and with carbon nanofibers isotropically distributed therein, which have a negative CTE along their axes. Now the actual properties of the Tokoro patent composite are impossible to calculate, as they effectively depend on the relative proportions of the components and wide ranges are given. However, one general property of the Tokoro patent composite that is ascertainable is that the overall CTE will be isotropic. In particular, either the overall CTE of the composite will be: a) dominated by the matrix, in which case the CTE will be positive in all directions; or b) dominated by the carbon nanofibers, in which case the CTE will (probably) be negative in all directions (particularly as the CTE in the axial direction will predominate, the CTE in the transverse direction being negligible relative to the axial direction). In either event, neither case corresponds to the claimed subject matter where the material of the balance spring "decreases in length and increases in thickness with an increase in temperature".

Therefore, for all of the foregoing reasons, it is submitted that the subject matter of independent claim 23 is neither disclosed nor made obvious by the Tokoro patent in view of the Baur patent so that claim 23 is allowable.

As the remaining claims 1-4, 6, and 9-22 have already been indicated as being allowable, it is submitted that the present application is in immediate condition for allowance and such action is solicited.

Respectfully submitted,

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## Thermal Expansion

The Physics Hypertextbook™  
 © 1998-2008 by Glenn Elert -- A Work in Progress  
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### Discussion

#### Solids

$$\begin{aligned}\Delta L &= L_0 \alpha \Delta T && \text{linear} \\ \Delta A &= A_0 2\alpha \Delta T && \text{superficial (areal)} \\ \Delta V &= V_0 3\alpha \Delta T && \text{volumetric}\end{aligned}$$

#### Liquids

$$\Delta V = V \beta \Delta T$$

Liquids have higher expansivities than solids

$$\beta \approx 10^{-3}/K, 3\alpha \approx 10^{-5}/K$$

#### Gases

[check out the [gas laws](#)]

behavior of gases is more complicated, gases will expand as much as pressure will allow

Coefficients of Thermal Expansion for Selected Materials

material	linear $\alpha$ ( $10^{-6} K^{-1}$ )	material	volume $\beta$ ( $10^{-6} K^{-1}$ )
aluminium	23.1	alcohol, ethyl	1120
barium ferrite	10	gasoline	950
brass	20.3	jet fuel, kerosene	990
carbon, diamond	1.18	mercury	181
carbon, graphite II	6.5	water, liquid (1 °C)	-50
carbon, graphite I	0.5	water, liquid (4 °C)	0
chromium	4.9	water, liquid (10 °C)	88
concrete	8 ~ 12	water, liquid (20 °C)	207
copper	16.5	water, liquid (30 °C)	303
germanium	6.1	water, liquid (40 °C)	385
glass	8.5	water, liquid (50 °C)	457
gold	14.2	water, liquid (60 °C)	522
iron	11.8	water, liquid (70 °C)	582
lead	28.9	water, liquid (80 °C)	640
nickel	13.3	water, liquid (90 °C)	695
platinum	8.8		
plutonium	54		
silicon	4.68		
silver	18.9		
solder, lead-tin	25		



# ASI Applied Sciences Inc.

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Home

## Research and Development Company

About ASI

ASI was founded in 1984 by researchers from the defense scientific community. ASI is a nationally recognized research and development company specializing in advanced materials and their applications. The ASI facility includes research and production areas and has employees comprised of top-notch scientists, engineers, and technicians who work with customers to meet their individual goals and needs.

Research

Affiliates

Approximately 75% of the activities at ASI are related to carbon nanofibers and composites in one form or another. For example, ASI has performed pioneering work in the development of vapor grown carbon nanofiber, and composites thereof, including polymer matrix, graphite/epoxy, carbon/carbon, and metal matrix composites. ASI fabricates carbon nanofibers using technology jointly developed between ASI and General Motors (specifically, General Motors Research and Delphi Chassis) under a licensing agreement. Essentially, these carbon nanofibers are related to the so-called Fullerene or C60 "buckyball" molecule led to the 1996 Nobel Prize in Chemistry for Robert F. Curl, Harold W. Kroto and Richard E. Smalley. Three different variations of nanofibers are of interest for producing electrically and thermally enhanced adhesives.

- **Pyrograf®-I** is a substrate grown fiber which attains lengths of up to 10 cm. Pyrograf-I has a larger diameter than Pyrograf-III and performs high thermal conductivity. It is useful in carbon pre-form or metal matrix composites for thermal management applications.
- **Pyrograf®-III** is grown completely in the gas phase, and tends to be grown in an entangled mass. It is now grown without any detectable pyrolytic overcoat. Pyrograf®-III may be properly referred to as a nanofiber. Pyrograf®-III is highly ordered without heat treatment (although heat treatment is still useful as a means of removing impurities, if desired).
- **Pyrograf®-IV** is similar to Pyrograf®-III, but contains an additional pyrolytic overcoat so that it attains a diameter of a few microns. Therefore, it is not properly referred to as a "nanofiber" but actually becomes a "microfiber." Because of its larger diameter, Pyrograf®-IV can be considered as an additive for high thermal conductivity.

The properties of the three Pyrograf® types are summarized below (incidentally, ASI does not offer a material called Pyrograf®-II. It was abandoned in favor of Pyrograf®-III by the mid 1990s). It is not practical to measure single-fiber

properties for very tiny fibers, but the strength, modulus, and CTE are inferred to be similar for all three materials (as measured for the case of Pyrograf®-I).

<b>Properties of PYROGRAF® Materials</b>			
Property	Pyrograf®-I (PR-I-HT)	Pyrograf®-III (PR-24-PS)	Pyrograf®-IV
Description	macroscopic fiber	nanofiber	microfiber
Ultimate Strength, GPa	7.0	7.0	7.0
Tensile Modulus, GPa	600	600	600
Diameter, microns	10	0.060 - 0.2	2,000
Length, microns	1 to 10 cm	100	100
Density, g/cm <sup>3</sup>	2.1	1.8	1.9
Pyrolytic layer thickness, nanometers	~500	~20	none
CTE, ppm *	-1.0	-1.0	-1.0
Electrical Resistivity, micro-ohm-cm	55	55	55
Thermal Conductivity, W/K-m	1950	TBD	TBD

\* Note that the coefficient of thermal expansion of these materials is slightly negative, in contrast to the polymer matrix, which usually expands significantly upon heating. Thermal expansion coefficient of polymer nanocomposites can be significantly reduced. Thus thermal strain is likely to be much lower in a polymer nanocomposite, which can be an important advantage for such materials.

ASI has an extensive data base on these carbon materials including different catalysts, substrates, and gas flow configurations for Pyrograf® fiber production; oxidation properties of carbon materials as a function of temperature; processing conditions for carbon nanomaterials for use in metal matrix, carbon matrix, and polymer matrix composites; measuring requisite properties of density, thermal conductivity, thermal expansion, and electrical conductivity.

Applied Sciences, Inc., is an advanced materials research firm fully equipped with development and complementary diagnostic facilities. In addition, ASI also has a carbon fiber production facility. While diamond production at ASI has heretofore been limited to research specimens, the production capacity is currently being scaled to accommodate prototype and pre-production units. ASI has over two dozen tube furnaces, analytical equipment includes light and scanning electron microscopes, gas chromatography, and apparatus for four-point probe electrical resistivity. An on-site machine shop supports fabrication of specialty parts and fixtures for research and production.

ASI has hot filament assisted CVD and microwave plasma assisted CVD Diamond reactors. Currently, diamond films, up to two inches in diameter, can be deposited on Si, Mo, and carbon/carbon composite substrates. Additionally, ASI can also coat tungsten

wire and carbon fiber with diamond thin films.

Please contact our Webmaster with any questions or comments.  
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